Metal release from contaminated estuarine sediment under pH changes in the marine environment

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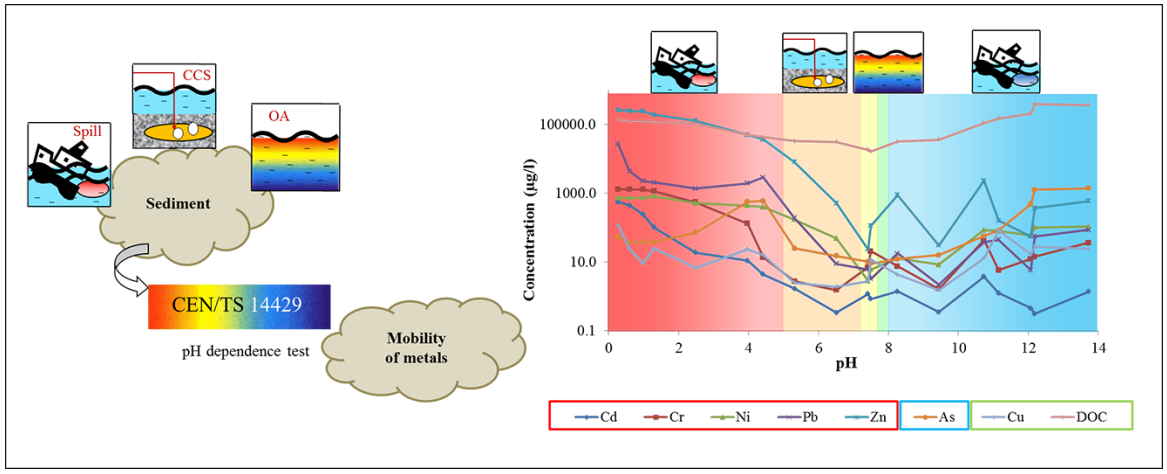
Graphical abstract



Abstract

The contaminant release from estuarine sediment due to pH changes is addressed using a modified CEN/TS 14429 pH dependence leaching test. The test is performed in the 0-14 pH range using deionised water and seawater as leaching solutions. The experimental

conditions mimic different circumstances of the marine environment due to the global acidification, CO_2 leakages from Carbon Capture and Sequestration technologies (CCS) and accidental chemical spills in seawater. Leaching test results using seawater as leaching solution show a better neutralisation capacity, giving slightly lower metal leaching concentrations than when using deionised water. The contaminated sediment shows a low base neutralisation capacity ($BNC_{pH=12}$=-0.44 eq/kg for deionised water and $BNC_{pH=12}$=-1.38 eq/kg for seawater), but a high acid neutralisation capacity when using deionised water ($ANC_{pH=4}$=3.58 eq/kg) and seawater ($ANC_{pH=4}$=3.97 eq/kg). Experimental results are modelled with the Visual MINTEQ geochemical software to predict metal release from sediment using both leaching liquids. Surface adsorption to Fe- and Al-(hydr)oxides was applied for all studied elements. The consideration of the metal-organic matter binding through the NICA-Donnan and Stockholm Humic Model (SHM) models for Pb and Cu respectively, improves the former metal release prediction. Modelled curves can be useful for the environmental impact assessment of seawater acidification due to its match with the experimental values.

Keywords: metal and As; sediment; seawater acidification; pH dependence test; geochemical modelling.

Highlights

- Metal release under natural ocean acidification, CO_2 leakages and accidental spills
- Equilibrium conditions at neutral pH using seawater are difficult to reach
- Salinity slightly decreases metals mobility from pH = 8
- Modelled metal release concentrations match well with the experimental ones
- Fe- and Al-(hydr)oxides and humic and fulvic acids improve metal release modelling

1. Introduction

Pressures and impacts on marine environments are a subject of environmental concern. In particular, the effects of human activities and climate change can, among other adverse effects, cause seawater pH variations. Global average oceanic surface pH has already declined by 0.1 since the beginning of the industrial revolution; modelled global ocean acidification predicts a pH decrease by another 0.2 to 0.77 units by the next two centuries (Table 1). Carbon capture and storage (CCS) is a very active field of research because of its potential to mitigate global warming (Pacala and Socolow, 2004; IPCC 2014). The projects with the highest total CO_2 storage estimation are offshore (Hosa et al., 2011). The pH value in environmental waters is used as one of the basic performance indicators to measure the possible impact of CO_2 storage and for the design of appropriate monitoring strategies to assess potential impacts of CO_2 seepage. A plethora of investigations exists about CO_2 leakages from CCS at different levels, as shown in Table 1 (References of this table are presented in the Supplementary Information). CO_2 leaks can cause short-time drops down to pH=3.0 in specific sea areas around the vents, showing high spatial and temporal variability in pH (Beaubien et al., 2008). In the case of marine chemical spills, pH values below 5 and above 12 have been reported for seawater areas directly surrounding the chemical spill location for a limited period of time (Gouriou et al., 2008; Mamaca et al., 2009).

69 **Table 1**. Estimated and measured pH changes on the marine environment due to the climate change,

70 leakages of CO_2 and chemical spills.

	Cause	Place	pH change effect
Climate change	Current global ocean acidification (OA). (Caldeira and Wickett, 2003). Modelled OA under several scenarios for proposed future CO_2 emissions. (Jeffree et al., 2009; Orr et al., 2005).	Global average oceanic surface pH.	pH has already declined by 0.1 units. pH decline by another 0.2 to 0.4 units by 2100 and by a maximum of 0.77 units at around the year 2300.
Leakages of CO_2 from natural storage and for CCS by injection into porous rock formations deep below the sea	Natural and industrial analogue sites from CO_2 storage reservoirs. (Beaubien et al., 2008; Gilfillan et al., 2009; Koornneef et al., 2012; Lewicki et al., 2007; Noble et al., 2012; Shitashima et al., 2008, 2013; Ziogou et al., 2013). (e.g.: Sleipner and Snøhvit offshore sites; Okinawa hydrothermal area).	Naturally occurring CO_2 reservoirs and natural gas storage sites analogues for the potential release of CO_2 from geologic storage sites.	Studies focused on: migration behaviour and fluxes of CO_2, transfer of gas to the atmosphere, seismic activity, reservoir characterisation, storage capacity and CO_2 dissolution in formation brine. pH of shallow waters: 5.48; pH of brine: 3.5; pH in the sediment pore water: 4-6.2.
	Laboratory experiments mimicking leakage from a sub-seabed CO_2 storage site and simulating "worst" case local scenarios of leakages. (Briffa et al., 2012; Cahill and Jakobsen, 2013; Carey et al., 2009; de Orte et al., 2014; Ellis et al., 2011; Jacquemet et al., 2009; Murray et al., 2013; Payán et al., 2012a, b; Widdicombe et al., 2013,2011).	Acidified seawater/ saline brine/ groundwater/ porewater at short-term (minutes to several days) contact with caprock formation/ sediment / environment.	In field scale injection experiments, pH is used as geochemical indicator of a leak. Various laboratories, start pH values (3.86, 4.4, 5.0, 6.5) depending on the simulated system, as the worst expected local scenario.
	Simulation models for a number of hypothetical leakage scenarios. (Amin et al., 2014; Bolourinejad et al., 2014; Zheng et al., 2009).	Model of the pH evolution, CO_2 plume, groundwater quality.	ΔpH=0.1-1.0 in seawater; Brine pH drop to 4.3; Initial cap rock formation water at pH=7.67 drops to pH= 3.0 at short time and stabilises at pH=5.8 at long time (Sleipner offshore field).
Accidental chemical spills	Acid chemical spill of 1700 t of sulphuric acid. (Mamaca et al., 2009).	Port of Río Grande, Brazil (low tide).	Chemical monitoring of pH (not reported data).
	Hydrodynamic and physicochemical simulation of an acid spill during the ECE incident (10,000 t of H_3PO_4 acid). (Gouriou et al., 2008).	Phosphoric acid spill in the English channel, west coast of France.	pH < 5 can be found in the area directly surrounding the spill location and only for a limited period of time.
	Alkaline chemical spill of 490 t of caustic soda from a barge. (Mamaca et al., 2009).	Bay of Newark, NJ, USA.	pH alongside the barge reached 12 very quickly and lowered to 9 three hours later.
	Accidental mining spill in Aznalcóllar. (Blasco et al., 2002; Gómez-Parra et al., 2000; Morillo et al., 2005; Riba et al., 2004,2002).	Spill affecting Guadalquivir estuary Gulf of Cádiz, Atlantic Ocean, Spain.	Spill of acid-polluted water at pH=4.5; estuarine sediment acidification down to pH= 6.5.
	Submarine acidic groundwater discharges to estuarine environments (Simpson et al., 2004)	Estuarine bays adjacent to industrial	Column leaching test experiments with acidified (HCl) groundwater solutions to pH 3, 4, 5.

		land. Sydney Harbour, Australia	
	In situ sediment solidification /stabilization (Renholds, 1998)	Several in-situ treatment projects	High pH values (pH=10) of sediments and surrounding area that results in a prevention of chemical release

Chemical additions or subtractions from the oceans can cause natural or human-induced seawater pH changes (Table 1). Broad pH changes could take place in local and short-term conditions, but in places where the pH may not rebound quickly to background conditions, or constituent concentrations of sediments in contact rebounded to values higher than the original background (Trautz et al., 2013). The major factors controlling the released concentrations for each metal are related to the solid matrix (sediments, marshes and caprock formations) characteristics, the fluid (seawater pH) characteristics and the solid-liquid contact characteristics (e.g. dilution, mixing degree and time following mixing) (Simpson et al., 2014). Changes in the pH of the seawater may increase metal mobility and availability from solid matrices in contact with seawater, that can result in irreversible, cumulative and interactive negative effects on specific sea areas around the vents and spill, with potential lethal and sublethal effects and metal bioaccumulation in the marine ecosystem (Ardelan et al., 2009; Briffa et al., 2012; Carrol et al., 2014; de Orte et al., 2014; Roberts et al., 2013).

In the context of ocean pH changes, information about the metal release from shallow sediment is essential for risk assessment and pre-incidental planning and can be used as a geochemical indicator of leaks. Therefore, the evaluation of the pH dependence of metal leaching is an important tool in the assessment of the expected long-term leaching behaviour of marine sediments in scenarios of ocean acidification as well as in extreme and/or accidental CO_2 leakages and chemical spills scenarios (Roberts et al., 2013).

Laboratory leaching tests, such as acidification using inorganic acids, in conjunction with routine sediment characterisations, can be used as cost-effective methods to predict constituent release, whose concentrations would rapidly rise at a field site due to the pH changes and important negative effects are expected at local scale. pH_{stat} leaching test based on CEN/TS 14429 has been widely used in different solid matrices of environmental interest as a powerful laboratory tool for the characterisation of

environmental samples (Table SI1-Supplementary information). The test complements and enhances the information derived from the use of common single extractions, and from other tests addressed to estimate the maximum leachability of inorganic pollutants. Although the pH_{stat} test may not be representative of in situ conditions, it can be environmental relevant when field tests are not possible or difficult to carry out, and useful to simulate worst case scenarios where acidified/alkalinised seawater is in contact with recent sediment from a potential CCS site or located in the area directly surrounding spill location, under total mixed conditions (Varadharajan et al., 2013; XXXXXXX).

This paper addresses the effect of pH on the leaching of As, Cd, Cr, Cu, Ni, Pb, Zn and Dissolved Organic Carbon (DOC) from contaminated estuarine sediment. The modified pH dependence leaching test with initial acid/base addition (CEN/TS 14429), covering the whole pH range (0-14), is done using deionised and seawater as leaching liquids. The use of different solutions allows to mimic different ocean acidification/alkalinisation conditions due to the current and modelled ocean acidification, CO_2 leakages from CCS technologies and accidental chemical spills.

Experimental research and geochemical modelling using Visual MINTEQ software were conducted to predict and explain the pH dependent leaching behaviour of contaminants; the proposed model considers surface complexation reactions on Fe- and Al-(hydr)oxides and bindings to dissolved organic matter through Gaussian, NICA-Donnan and Stockholm Humic Model (SHM). This model approach expands the previous developed model (Payán et al., 2012a,b) providing more accurate information to assess the risk related to metals release from marine sediments exposed to changes in pH.

2. Materials and experimental method

2.1. Sediment sample collection and characterisation

All sampling and laboratory material was pre-cleaned, acid washed (10% HNO_3) and rinsed with Milli-Q water (Direct-Q 5 UV, Merck Millipore). The estuarine surface sediment samples were collected in November 2011 from the estuary of Suances (Northern Spain) a narrow and shallow mesotidal estuary, with 5.5 km long and a 150 m mean width (surface area of 389 ha, 76% of which is occupied by intertidal flats). Land reclamation has reduced the original estuarine area by 30%, while 50% of the estuary is bordered by dikes (over 13000 m) (Bárcena et al., 2011). The estuary of Suances should be classified as highest priority site with regard to its pollution with very high levels of Pb and Zn and high toxicity in the whole estuary and the specific site selected in this work, nearest to the sea, is representative of the whole estuary (Álvarez-Guerra et al., 2008). The estuary, is part of an area that has been classified as a potential receiving site of Carbon Capture and Sequestration (CCS) techniques, by the Spanish Government (BOE, 2008).

A detailed description of the methodology used to determine the crystalline sediment phases, the total metal content and the organic carbon of the sediment is presented in the Supplementary Information.

The amounts of Fe- and Al-(hydr)oxides were estimated in duplicate by the sodium dithionite-sodium citrate with $NaHCO_3$ buffer system method (Mehra and Jackson, 1960). Selective chemical extractions were performed in duplicate on the sediment to determine the amounts of humic acids (HA) and fulvic acids (FA). The humic and fulvic fractions were determined with a batch method derived from the currently recommended

150 procedure of the International Humic Substances Society (IHSS) (Swift, 1996; Thurman
151 and Malcolm, 1981).
152
153 **2.2. Leaching tests**
154 The pH dependence leaching test with initial acid/base addition, as described in the
155 standard CEN/TS 14429, was performed in duplicate with some modifications. Two set
156 of experiments with deionised water and seawater where performed, with predetermined
157 amounts of acid (HNO_3) or base (NaOH) added to subsamples at L/S=10 l/kg at 10 rpm
158 for 48 h in three stages at 0, 30 and 120 minutes (t_0, $t_{0+30min}$, t_{0+2h}). The pH of the leachate
159 was measured after each stage and the equilibrium at the end of the experiment verified.
160 It was considered that the equilibrium was achieved if the difference between pH_{44h} and
161 pH_{48h} was smaller than 0.3. Moreover this test allows to obtain the acid and base
162 neutralisation curve which is useful to know the quantity of acidification needed to reach
163 a determined pH value. Whole pH range (0-14) to mimic potential environmental risks
164 situations, as ocean acidification by natural or anthropogenic CO_2 leakages and potential
165 chemical spills, have been used. This approach using wider range of pH that standard, has
166 been apply previously by different authors (Table SI1 Supplementary Information).
167
168 Each leachate sample obtained at the end of the experiment, was filtered through a 0.45
169 μm pore size nitrocellulose filtration membrane and divided in two subsamples: one for
170 measuring the pH using a pH meter equipped with a suitable electrode for samples with
171 suspended solids and for determining DOC by the high temperature combustion method;
172 the other subsample was acidified to determine Cl^- by titration and As, Cd, Cr, Cu, Ni,
173 Pb, Zn concentrations by an Agilent 7500CE ICP-MS equipment using He collision
174 mode. All analyses were carried out in duplicate. A detailed description of the pH

175 dependence leaching test performed, as well as of the analysis of the leachates is presented
176 as Supplementary Information.
177
178 **2.3. Modelling of metal leaching data using Visual MINTEQ software**
179 Geochemical modelling was carried out using the software Visual MINTEQ (ver. 3.0)
180 (Gustafsson, 2012). The model input files were composed of the maximum concentration
181 obtained in the modified CEN/TS 14429 of the elements of interest (As, Cd, Cr, Cu, Ni,
182 Pb, Zn) and of the inorganic carbon (CO_3^{2-}) as well as of the major components (Al^{3+},
183 Ba^{2+}, Ca^{2+}, Mg^{2+}, Si^{2+} and Fe^{3+}) and metal binding ligands (PO_4^{3-}, SO_4^{2-} and SO_3^{2-}) of the
184 sediment under study. Possible solid phases of the major components and the considered
185 elements of the sediment were selected based on experimental analysis of previous studies
186 (Payán et al. 2012a,b).
187
188 Surface complexation and bindings to organic matter were considered using sequentially
189 the available models in the software. Adsorption on Fe- and Al-(hydr)oxides was taken
190 into consideration whereas the Gaussian, NICA-Donnan and Stockholm Humic Model
191 (SHM) were used to assess metal binding to organic matter.
192
193 The ionic strength and the concentration of the major ions (Na^+, Cl^-, SO_4^{2-} and Mg^{2+}) of
194 seawater were also considered to model the metal behaviour when seawater was the
195 leaching liquid. Visual MINTEQ was successfully used to model metals behaviour in
196 saline waters (Cidu et al., 2013; Gabrijel et al., 2009) and marine waters (Åstrom et al.,
197 2012; Ndungu, 2012).
198
199 **3. Results and Discussion**

3.1. Sediment sample characterisation

Quartz, aluminium oxide, calcite and dolomite are the principal crystalline phases in the studied sediment whereas Pb and Zn are the trace elements that are present in the highest concentrations. The selective chemical extractions performed on the sediment show that it contains 15.14±0.44 mg/g of Fe (hydr)oxides, 1.67±0.02 mg/g of Al-(hydr)oxides, 120.9±37.2 mg/kg of humic acids and 790.5±23.2 mg/kg of fulvic acids. Detailed description of the sediment characterisation results is presented in the Supplementary Information.

Although the sampled sediment is considered superficial because the maximum depth is about 10 centimetres it is supposed to be a reduced sediment due to the black and not grey colour and the negative redox potential, presenting values as low as -130 mV. In many sediments, redox zonation is not clear, and oxic (oxyhydroxides) and anoxic (sulphide) phases coexist at that depths (Burdige, 1993; Williamson et al., 1999; Simpson et al., 2000).

3.2. pH dependence leaching test results with deionised water and seawater

The pH curve obtained from the pH titration helps to predict changes in the pH of a sample when affected by acidic or basic stresses (Rigol et al., 2009). Figure 1 shows the changes in pH after the addition of acid (positive scale) or base (negative scale) in a deionised and seawater environment. The experimental results show that the sediment has a low neutralisation capacity to base addition ($BNC_{pH=12}$=-0.44 eq/kg when using deionised water and $BNC_{pH=12}$=-1.38 eq/kg for seawater), but a relatively high acid neutralisation capacity ($ANC_{pH=4}$=3.58 eq/kg for deionised water and $ANC_{pH=4}$=3.97 eq/kg for seawater), due to its high carbonate content. The buffering capacity of the seawater also

influences the test because a higher amount of acid or base is needed to achieve the same pH value when seawater is used. This buffering capacity is the result of the consumption of H^+ and CO_2 by reaction with CO_3^{2-}, counteracting much of the H^+ and CO_2 increase (Egleston et al., 2010).

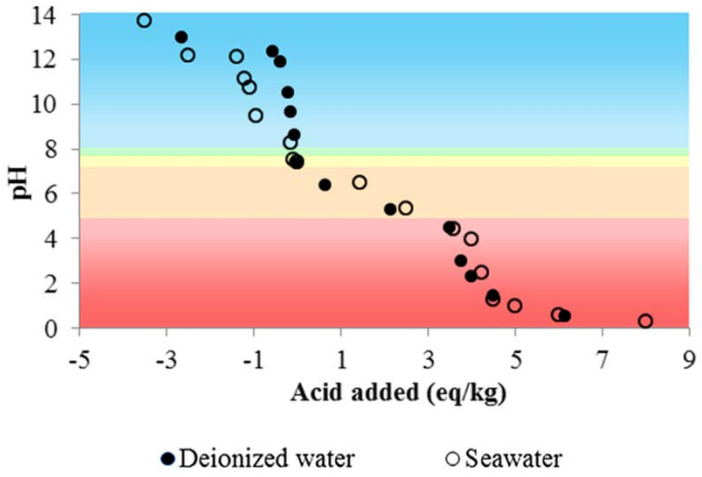


Fig. 1 pH *vs.* eq/kg of added acid in the pH dependence leaching test when using deionised water and seawater. The bands represent different local potential situations under: alkaline chemical spills (pH>8) in colour blue; natural seawater (pH: 8-7.9) in colour green; ocean acidification (pH: 7.9-7.2) in yellow; leakages from a CO_2 storage site (pH: 7.2-5) in orange and under acid chemical spills (pH<5) in red

Some difficulties were found to achieve samples which reach the test equilibrium conditions (defined as pH_{48h}-pH_{44h}=$\Delta pH_{eq.}$<0.3), especially working with seawater around the neutral pH. It shows that a 48 h experiment might not be sufficient for a thorough assessment of metal leaching; thus longer time tests (96 h) were performed to check the equilibrium at different periods of time. For the studied sediment, the performance of longer time tests did not help to reduce the number of samples necessary to achieve the equilibrium condition ($\Delta pH_{eq.}$<0.3); moreover, the use of longer times decreased the final pH in the basic zone and increased it in the acidic zone, slowly neutralizing the initial pH value due to the buffer capacity of the seawater used as leaching

244 agent. Details related to the pH difference to reach the equilibrium, number of samples
245 performed and pH evolution with time, are included in the Supplementary Information.
246
247 This shows that the natural environment tends to reduce the external modifications
248 although some hard stresses, like CO_2 leakages due to CCS technologies and chemical
249 spills, could not be totally absorbed. Furthermore, and because of the minor differences
250 found in the experimental results, it is concluded that 48 hours of experiment is enough
251 to evaluate the contaminant release from this polluted sediment in several pH
252 environments in contact with deionised water and seawater.
253
254 **3.3. Metal and DOC release for pH dependence leaching test with deionised water**
255 **and seawater**
256 The release of cations from solid matrices is to a large extent determined by the release
257 of Dissolved Organic Carbon (DOC) (Dalgren et al., 2011). Figure 2 shows the DOC
258 (mg/l) release during the pH dependence leaching test.
259
260 For both leaching solutions, DOC releases at acidic conditions probable due to the
261 solubility of FA at low pH values (Cappuyns and Swennen, 2008), reaching minimal
262 concentration at neutral pH value (15 mg/l). From this pH value, DOC increases
263 exponentially with pH due to the higher negative charges on both organic matter and soil
264 inorganic solid surfaces so that these repel each other (You et al., 1999). This exponential
265 increase of DOC at basic pH values is smaller when using seawater as liquid solution.
266 This might be due to the weaker electrical repulsion force experienced by the organic
267 molecules (mainly humic and fulvic acids) interaction with the sediment surface (Münch
268 et al., 2002).

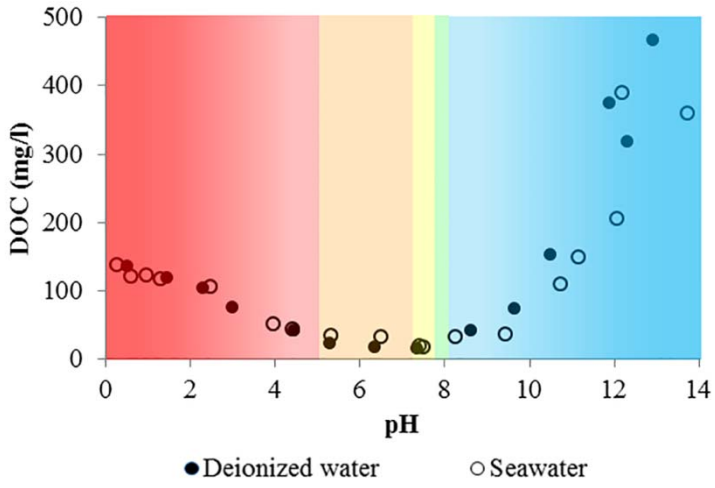


Fig. 2 DOC (mg/l) experimental release with pH for deionised water and seawater

The influence of pH on metal leaching from the studied sediment is emphasised by the large changes in the release concentration results (Fig. 3). Metal leaching for deionised water and seawater presents similar results and tendencies, showing a slightly higher release in the case of deionised water, especially in the basic range.

The pollutant As (Fig. 3) behaves like an oxyanion, showing not only a minimum but also a maximum concentration and a high release at basic pH due to the negatively charged surfaces above the point of zero charge, when the sorption of anions is less favourable (Rigol et al., 2009). The maximum leaching for Cr, Ni, Pb and Zn is observed in the pH range 0-4, which is consistent with the observation that at acidic pH the solid surfaces are positively charged and metal sorption is not favoured. Metal release decreases until minimum values at pH between 6 and 10 and increases again in the alkaline pH range, probably as a consequence of the dissolution of organo-metallic complexes (Almås et al., 2000; Güngör and Bekbolet, 2010; Impellitteri et al., 2002).

287 Cu shows a more similar behaviour to DOC than the other elements. Cu sorption is weak
288 at low pH, increases with increasing pH, presenting the maximum sorption, and as a
289 consequence the minimum release, at pH 5-9. Cu sorption decreases at basic pH values
290 probably because of inorganic and organic complexation of Cu in solution (Impellitteri et
291 al., 2002; Rigol et al., 2009; Strobel et al., 2001). Also Pb seems to have a high degree of
292 complexation with DOC; both metals have a relative to Ni, Zn and Cd higher affinity for
293 specific binding to humic substances (Ahmad et al., 2012; Buffle, 1988; Milne et al.,
294 2003). Hence it is shown that the release of Cu and Pb at high pH values using seawater
295 is lower than when using deionised water as leaching liquid according to the lower
296 quantity of DOC in the seawater experiments.
297

298 **3.4. Geochemical modelling of the metal release for pH dependence leaching tests**
299 **with deionised water and seawater**

300 During the assay, the oxidation of different compounds, S^{2-} included, happens. The
301 reasons for this process are the absence of an inert atmosphere, the contact of some air
302 with the sediment-sample inside the bottle (headspace) and the intrusion of air when the
303 recipient is opened to add the needed acid or base and to measure the pH.
304

305 As a consequence of this oxidation, an increase in the redox potential, achieving positive
306 values, and a colour change in the sediment (being brown-yellow) are appreciated. These
307 two reasons allow us to think that oxidation of sulphide during the leaching tests can
308 cause these changes.
309

310 Additionally, an in order to verify that these changes are produced because of the presence
311 of oxygen, additional experiments were carried out in the laboratory (see Supplementary
312 information).
313
314 Although it is known that metals bind stronger with sulphide phases than with carbonate,
315 Fe- or Mn-(hydr)oxides or particulate organic carbon (Simpson et al., 2004), these
316 compounds are kinetically stable only over periods of some hours (Simpson et al., 1998).
317 Hence, the longer duration of the assay under study (48 h) allows all the sulphides to be
318 oxidised. During the oxidation process the S^{2-} becomes to sulphates while dissolved metal
319 concentrations increases due to their release (Simpson et al., 2000).
320
321 As the geochemical model is done in equilibrium conditions (t=48 hours), all the S is
322 expected to be oxidised. As mentioned in the methodology section S is taken into account
323 as SO_4^{2-} and SO_3^{2-} in the geochemical modelling to represent the complete oxidation of
324 all sulphide compounds.
325
326 The previous decision is also supported because in contaminated sediments, high
327 proportions of Zn and Pb may not be present as metal sulphides, even when elevated
328 sulphide concentrations are present (Simpson et al., 2000). Zn and Pb can also be
329 incorporated as trace elements in Fe-monosulphides and pyrite (Brennan and Lindsay,
330 1996). However, Pb, Zn and Cd are generally only pyritized to a few percent, as a
331 consequence of the precipitation of metal-sulphide phases prior to FeS formation and
332 subsequent pyrite formation (Morse and Luther, 1999).
333

Although it was reported that under conditions in which there is an abundance of SO_4^{2-} compared to Fe the control by pyrite (FeS_2) would have no effect (Brennan and Lindsay, 1996), the influence of this phase was tried in the geochemical software. Other metal sulphides such as chalcopyrite ($CuFeS_2$), galena (PbS), mackinawite ($(Fe,Ni)_{1+x}S$) or chalcocite (Cu_2S) were introduced in the geochemical software to verify their influence and assess the assumption that all the S was oxidised in the experimental assay. Another phases like tennantite (Cu_3AsS_3), enargite (Cu_3AsS_4) (Wildeman) or pyrrhotite ($Fe_{1-x}S_x$) (Balistrieri et al., 2007; Chapman et al., 1998; Zhuang et al., 1994) could not be considered because we did not find the formation constants to add them to the database of the software. Predicted curves did not change, or even were worse, so it could be concluded that the shown predicted curves are the most reliable under complete oxidation conditions. Even if experimentally it would not happen, its consideration allow to obtain the most conservative values and avoid the environment to be damaged due to the higher predicted release of the elements under study as a consequence of the consideration of the complete oxidation.

For modelling purposes, the sum of Fe- and Al-(hydr)oxides, due to the absence of a database for adsorption on aluminum(hydr)oxides, was considered as solid adsorbent. Among the different models available in the software, the Generalised Two Layer Model (GTLM), named HFO, provided by Dzombak and Morel (1990) and the Fh 3-site (Gustafsson et al., 2011) are those which best fit with the experimental values. The match between experimental and modelled results are better using the HFO model in the case of Cr, Cu and Zn and the Fh 3-site model for Cd, Ni and Pb.

358 The effect of pH and salinity, especially at basic pH values, on the organic matter
359 motivated to accomplish a modelling strategy which considered DOC models for all the
360 elements studied; however, the influence of DOC on the release of metals was expected
361 to be higher in the case of Cu and Pb (Sundaray et al., 2011; Yap et al., 2002).
362
363 Figure 3 shows the metal leaching and geochemical modelling results for the pH
364 dependence leaching test in the whole pH range using deionised water and seawater as
365 leaching solutions.
366
367 Arsenic is the only element whose modelled release without and with adsorption (HFO
368 model) is shown (Fig. 3). When adsorption is not considered, As precipitates as
369 $BaHAsO_4H_2O$ at pH: 6-12 using deionised water and at pH: 7-11 when seawater is the
370 leaching liquid; the best match between modelled and experimental curves is at pH≥11.
371 However, the model overestimates the release at acidic conditions. Considering that it
372 could be due to the adsorption to Fe- and Al-(hydr)oxides, results including the HFO are
373 also shown (Fig. 3). The match at pH≥11 is also good so adsorption is not the controlling
374 factor at high pH values (Mamindy-Pajany et al., 2009). Moreover, these modelled curves
375 have the same pattern that the experimental release, including the maximum at pH=4, but
376 underestimate it in three orders of magnitude. Experimentally there is not as much
377 adsorption as the model predicts, probably due to a higher competition between As and
378 ubiquitous anions such as SO_4^{2-}, CO_3^{2-} and Cl^- (Cornelis et al., 2012) than the one
379 considered by the model.
380
381 An increase in acidity does not have an important effect on the mobility of Cd, a typically
382 mobile element, whereas for Ni, Pb and Cr, typically fixed elements, an increase in acidity

causes a considerable increase in extractability as has been reported previously by Sauquillo et al., 2003. The main solid phases in Cd model are $Cd(OH)_2$ and $Cd_4(OH)_6SO_4$ at basic pH values. The adsorption is an important phenomenon which improves the prediction of its release, especially at basic pH values and using the Fh 3-site model. Nevertheless, the model overestimates the release even in three orders of magnitude at pH<8. The influence of the organic matter was evaluated using the three available models in the software but predicted curves did not match better with the experimental one. Variation of Cd speciation in sediments has been reported as more significant than other elements. In fact, total Cd concentration was observed in exchangeable fraction, in easily reducible fraction and noticeable portion of Cd was found in residual fraction bound in lithogenic minerals (Cuong and Obbard, 2006; Nemati et al., 2011). Thus, the overestimation could be explained by the influence of clay, silt fractions and oxidic and layer silicate surfaces in Cd sorption (Harichandan et al., 2013; Naidu et al., 1997), not included in the database of the software.

The adsorption of Cr on the Fe- and Al-(hydr)oxides occurs in almost the whole pH range using the HFO model. The main solid phase is Cr_2O_3, present at pH values higher than 9 for both leaching liquids. Some experimental values in the pH range of 5-10 are below the detection limit so modelled results might be considered an approximation. Under this model scenario a good description of Cr leaching in the full pH range is obtained.

For Cu, the modelled release pattern shows a minimum release at neutral pH values due to the use of the adsorption (HFO) and the SHM model which considers the dissolution and precipitation of humic and fulvic acids. The modelled curve using seawater (dotted line in Fig. 3) is not complete because the software is not able to present a result at some

408 pH values due to the complexity of the model and the reach of the maximum number of
409 iterations.
410
411 The modelled results for Ni using Fh 3-site model show that $Ni(OH)_2$ is the controlling
412 phase for Ni at basic pH values (pH $\geq$10) as concluded by Dijkstra et al. (2004) and Payán
413 et al. (2012a). The software indicates that the maximum concentration of Ni adsorbed on
414 Fe- and Al-(hydr)oxides occurs in the pH range 7-10 for the two surface adsorption
415 models used.
416
417 According to the modelled curves, Pb may precipitate as chloropyromorphite(c)
418 ($Pb_5(PO_4)_3Cl$) at pH 5-10. In addition to including the Fh 3-site model, the modelling of
419 this element takes into account the metal-DOC binding by the NICA-Donnan model,
420 which uses the experimental humic and fulvic acids. This model scenario provides a good
421 description of Pb under sediment resuspension conditions and ocean acidification due to
422 the climate change and leakages of CO_2, but overestimates Pb leaching at high pH values.
423
424 Modelled by HFO, Zn precipitates as smithsonite at neutral pH values (6-8) and as zincite
425 at pH values higher than 10. As shown by Zhang et al. (2008), the consideration of the
426 surface adsorption does not have an important influence on Zn release although the curves
427 improve taking it into consideration.

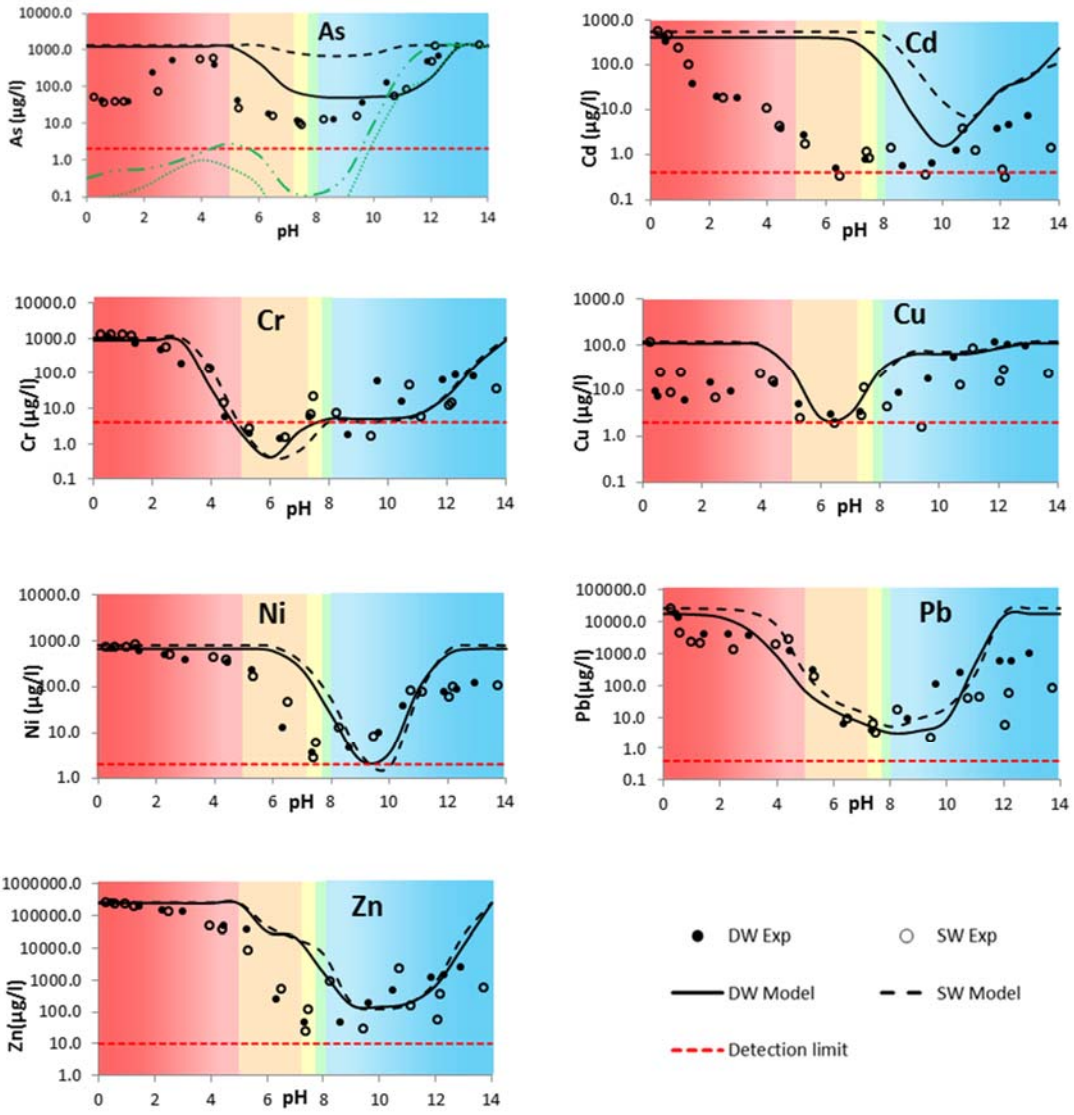


Fig. 3 Experimental (Exp) and modelled results of metal leaching as a function of pH for the pH dependence leaching test using deionised water (DW) and seawater (SW) as leaching solutions. In the case of As, black curves represent results without adsorption to Fe- and Al-(hydr)oxides whereas the green ones including it (·····DW; — ·· — SW)

4. Conclusions

Contaminated sediment samples from the potential CO_2 store site of Suances (Spain) are subject to modified pH dependence leaching test using deionised water and seawater as leaching solutions in the whole pH range.

438 Experimental results confirm that DOC release depends on pH as well as the type of water
439 used. Metal leaching for deionised water and seawater presents similar concentrations
440 and tendencies, although it is slightly higher when using deionised water especially at
441 high pH values.
442
443 The pH-dependent leaching behaviour predicted by Visual MINTEQ agreed well with
444 the analytical values being a useful model to determine metal species in solution over a
445 large pH range in seawater. These results would be helpful to the pre-incidental planning
446 of the environmental impact assessment in the sea area directly surrounding the CO_2
447 leakages and under different scenarios of acidification and/or alkalinisation of seawater.
448 The organic complexation of humic and fulvic acids and the adsorption to Fe- and Al-
449 (hydr)oxides are the main mechanisms that can explain the leaching behaviour; however,
450 results of As and Cd make us consider further studies of sediment mineralogy, clay
451 contents and crystallinity to include them in geochemical software. Due to the difficulties
452 found to achieve the equilibrium condition, the evaluation of metal release under the
453 influence of pH with continuous control is proposed as future work.
454
455 In order to verify and know exact quantities of the oxidation process, a sequential
456 extraction in combination with the kinetic evaluation of metal release under the influence
457 of pH with continuous control, is proposed as future work to assess the change of
458 speciation.
459
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